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Energy-induced dual curable compositions.

An energy polymerizable composition comprises at least one ethylenically unsaturated monomer, one of polyesterurethane precur's, and at least one epoxy monomer, and a curing agent comprising an organosilicic compound and an oxum salt.

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ENERGY-INDUCED DUAL CURABLE COMPOSITIONS

FIELD OF THE INVENTION

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This invention relates to an energy-polymerizable composition comprising an ethylenically-unsaturated monomer and either polyurethane precursors or an epoxy monomer, and as curing agent a combination of monomer and either polyurethane precursors or an epoxy monomer, and a method thereof in a further aspect, cured in an organometallic compound and an oxidizing agent; the compositions are useful for articles comprising the composition of the invention are disclosed. The compositions are useful, for example, as protective coatings, binders for magnetic media or abrasives, adhesives, and in graphic arts applications.

Background Of The Invention

Backgrounds of the Process

Various polymeric coatings and adhesives are produced in processes involving the use of organic solvents. There is an intense effort by law makers, researchers, and industry to promote high and 100% solids formulations to reduce or eliminate the use of such solvents and the attendant costs and environmental contamination. These processes require a latent catalyst or latent reaction promoter which can be activated in a controlled fashion.

Various promoters using reaction promoters such as tin salts and barium salts have been used to reduce undesirable

Thermal curing of polyurethane precursors with polyisocyanates with polyurethane precursors is known in the art. Curing of polymerizable mixtures of polyisocyanates with polyurethane precursors is known in the art (see for example U.S. Patents 4,521,345, and 4,562,081).

[illegible]

The dual curing of acrylate urethane precursor mixtures is known but these curing methods are not disclosed. The dual curing of acrylate urethane precursor mixtures is known but these curing methods are not disclosed. The dual curing of acrylate urethane precursor mixtures is known but these curing methods are not disclosed.

entirely produced in the United States. _____
 precursors and copolymers (see U.S. Pat. 4,342,783 and Mosser, _____
 pages 46-55). _____
 processes for the polymerization of epoxy materials. It is further known that a _____
 (U.S. Patent No. _____)

[illegible]

4. Polymerization Furthermore, the above-mentioned U.S. Patent No. 4,194,268 teaches the thermal curing of elastomeric polymers containing organic salts and reducing agents. Radiation-curable curable compositions containing ethylenically unsaturated monomers and epoxy monomers have been described in U.S. Patent Nos. 4,194,035, 4,221,978, and 4,823,878. These compositions may include organic salts combined with organic compounds as the curing agent, but do not contain inorganic salts.

Energy polymerizable compositions comprising one kind or more than one organic monomer. Energy polymerizable compositions comprising one kind or more than one organic monomer and the curing thereof has been taught (see European Patent Application number 006,418, 1983). Current abstract: 006,418, 1983.
Waxes 108,251 1984 Current abstract: 004,915, 1983. Current abstract:
abstract:

Neutral organometallic compounds have been used in conjunction with
for the photocuring of ethylenically-unsaturated monomers (D. Smith, A.
113611). M. M. Wagner, M. D. Furutachi, J. Photolith. Science, **29**, 230-236,
of certain photoresist materials with certain salts for initiation

[illegible]

Summary of the meetings

Briefly, the present invention provides an ethylenically-unsubstituted polymer (U.S. Pat. 2,940,711) and an ethylenically-unsubstituted monomer and ester polymer (U.S. Pat. 2,940,712) for curing against a combination of a organosolastic compound, such as an organosolastic compound, as protective and decorative coatings, resins, adhesives, binders, etc., as well as for use in a variety of other applications, and in many applications.

It is believed not known in the art that using, in combination with an ethylenically-unsubstituted monomer, an organosolastic compound, for curing against a combination of an organosolastic compound and an ethylenically-unsubstituted monomer, can be achieved by using as curing agent a combination of an organosolastic compound and an ethylenically-unsubstituted monomer.

Advantages of Conversions of the present technology

1. Some methods involving process innovation is discussed that will reduce the molecular weight of solvent waste while reducing energy consumption.
2. Radiation processing, particularly utilizing electron beam and γ radiation, is capable of generating and polymerizing such and experimental work is being done. More readily available monomers can be used in place of butadiene thereby resulting in lower viscosity monomer solutions which are solutions.
3. Expanding the scope of curable monomers to include α,β -unsaturated ketones with specific properties.

increase steadily in varying degrees.

In this application:

"Oxid Curing" means the small/medium energy-induced curing combination with one of polyesters/epoxies and epoxy resin.

"Energy-Induced Curing" means curing by means of the combination of "energy-induced particles (including electron beam, and infrared/ultraviolet/visible light) and chemical catalysts."

"Thermally Unstabilized Resin" means those resins that are thermally unstable and require a chemical catalyst to effect a "catalytic-curing process" means a quantity of catalyst is added to a polymerized product in order to degrade to cause an effective "catalytic-curing process" means a chemical stabilization in which the catalyst is added to the resin.

"Organometallic Compound" means a chemical stabilization in which the catalyst is added to the resin.

[illegible]

Neutral organometallic compounds have been used in combination with neutral halogenated compounds for the photocuring of ethylenically-unsaturated monomers (G. Smets, Pure G. Appl. Chem. 53, 611-615, 1981); M. Wagner, M.D. Putzbach, J. Photogr. Sci. 29, 230-235, 1981).

The use of certain photosensitizers with rhenium salts for initiation of polymerization of ethylenically-unsaturated monomers is also well known in the art. This technique has found applications in printing, lithography, copying and other imaging systems (see J. Kozal in Light Sensitive Systems, Chemistry and Application of Nonlinear Halide Photographic Processes, Wiley, New York, 1985, pp. 158-193). Arylodonium salts have been previously described for use as photoinitiators in addition-polymerizable compositions (see U.S. Patent Nos. 3,729,313, 3,741,769, 3,808,006, 4,228,232, 4,250,053 and 4,428,807; H. J. Timpe and H. Baumann, Wiss. Z. Tech. Hochschule Leuna-Merseburg 28, 439 (1984); H. Baumann, B. Strehmel, H. J. Timpe and U. Lammert, J. Prakt. Chem. 326 (3), 415 (1984); and H. Baumann, U. Dörrle and H. J. Timpe, Euro. Pat. J. 22 (4), 313 (April 3, 1986)).

Summary of the invention

Briefly, the present invention provides an energy polymerizable composition comprising an ethylenically-unsaturated monomer and either polyurethane precursors or an epoxy monomer, and as curing agent a combination of an organometallic compound and an onium salt. The compositions are useful as protective and decorative coatings, inks, adhesives, binders for magnetic media or abrasives, in restorative and sealant applications, and in imaging applications.

It is believed not known in the art that latent, energy induced, simultaneous, preferably solventless dual curing of ethylenically-unsaturated monomers, in combination with either polyurethane precursors or epoxy monomers, can be achieved by using as curing agent a combination of an organometallic compound and an onium salt oxidizing agent.

Advantages of compositions of the present invention when utilized in 100% reactive coating compositions include:

1. An industrial process innovation is disclosed that will reduce, minimize, or eliminate the generation of industrial solvent waste while reducing energy consumption.
2. Radiative processing, particularly utilizing electron, beam and photogenerated catalysts, has potential capability for penetrating and polymerizing thick and pigmented coatings.
3. More readily available monomers can be used in place of functionalized oligomers (used in the prior art) thereby resulting in lower viscosity monomer solutions which are easier to coat than more viscous oligomer solutions.
4. Expanding the scope of curable monomers to include polyisocyanates polyols and epoxides allows increased flexibility in designing coatings with specific properties.

In this application:

- 1. "dual curing" means the simultaneous energy-induced curing of ethylenically-unsaturated monomers in combination with one of polyurethane precursors and epoxy monomers;
- 2. "energy-induced curing" means curing by means of electromagnetic radiation (ultraviolet and visible);
- 3. "accelerated particles (including electron beam), and thermal (infrared and heat) means;
- 4. "ethylenically unsaturated monomer" means those monomers that polymerize by a free-radical mechanism;
- 5. "ethylenically-effective amount" means a quantity sufficient to effect polymerization of the curable composition to a polymerized product at least to a degree to cause an increase in the viscosity of the composition;
- 6. "ion to a polymerized product at least to a degree to cause an increase in the viscosity of the composition;
- 7. "organometallic compound" means a chemical substance in which at least one carbon atom of an organic group is bonded to a metal atom ("Basic Inorganic Chemistry", F. A. Cotton, G. Wilkinson, Wiley, New York, 1978, p. 487);
- 8. "polyurethane precursors" means a mixture of one or more monomers of the type including diols and polyols. Compounds and polyisocyanates, and one or more monomers of the type including diols and polyols, the ratio of bearing at least two isocyanate-reactive hydrogen atoms is 1:2 to 2:1;
- 9. "bearing at least two isocyanate-reactive hydrogen atoms is 1:2 to 2:1";
- 10. "of isocyanate groups to isocyanate-reactive hydrogen atoms is 1:2 to 2:1";
- 11. "polymerizable mixture" means a mixture where the ratio of (ethylenically-unsaturated compounds) (polyurethane precursors or epoxy compounds) is 1:99 to 99:1;
- 12. "bridging ligand" means a ligand that bonds to two or more metals in the presence or absence of metal-metal bonds;
- 13. "metal bonds";

"polyacrylate" means an aliphatic or aromatic isocyanate having 2 or more isocyanate groups.
 "polyol" means an aliphatic or aromatic compound containing 2 or more hydroxyl groups, and
 "curium salt" means salts of curium compounds such as dacturium, halonium, and hypervalent Group VIA elements.

Detailed Description of the Invention

- above specifically, in a preferred embodiment the invention describes an energy polymerizable composition comprising in the range of 80 to 1 weight percent an ethylenically-unsaturated monomer and 1 to 80 weight percent of either polyurethane precursors or an epoxy monomer and a b-component curing agent thereby, the curing agent comprising

1) an organometallic compound having the structure

15 L₁L₂L₃M

wherein

- L₁ represents none, or 1 to 12 ligands contributing p-electrons that can be the same or different ligands selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic, aromatic and heterocyclic aromatic compounds, each capable of contributing 2 to 12 p-electrons to the valence shell of M;
 L₂ represents none, or 1 to 24 ligands that can be the same, or different contributing an even number of p-electrons selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons to the valence shell of M;
 L₃ represents none, or 1 to 12 ligands that can be the same or different, each contributing no more than one sigma electron each to the valence shell of each M;
 M represents 1 to 4 of the same or different metal atoms selected from the elements of Periodic Groups IIA, VIIA, VIIIA, and VIII (commonly referred to as transition metals);

- with the proviso that said organometallic compounds contains at least one of a metal-metal sigma bond and L₁ and with the proviso that L₁, L₂, L₃ and M are chosen so as to achieve a stable configuration, and
 2) an curium salt containing agent having the structure B

16 A₁ X

wherein

- A is an organic cation selected from those described in U.S. Patent Nos. 3,708,288, 3,729,313, 3,741,788, 3,784,578, 3,800,008, 4,028,705, 4,028,401, 4,088,055, 4,101,513, 4,218,288, 4,394,403, and 4,623,678, preferably selected from dacturium, iodonium, and subonium cations, while more preferably A is selected from dacturium, dacturium, and phenylthiophenyl dacturium, and
 X is an anion, the cation of the curium salt including those in which X is an organic anion, or an inorganic anion or substituted, such as CH₃SO₃⁻, CF₃SO₃⁻, C₆H₅SO₃⁻, p-toluenesulfonate, p-chlorobenzenesulfonate and related anions and the like, and
 wherein D is a metal from Groups IB to VIII or a metal or metalloid from which X has the formula DZ, wherein D is a metal from Groups IB to VIII or a metal or metalloid from Groups IIA to VA of the Periodic Chart of Elements, Z is a halogen atom, and r is an integer having a value of 1 to 6. Preferably the metals are copper, zinc, titanium, vanadium, chromium, manganese, iron, cobalt, or nickel and the metalloids preferably are boron, aluminum, indium, tin, arsenic, and phosphorus. Preferably the halogen, Z, is chlorine or fluorine. Substituents of suitable anions are BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, FeCl₄⁻, SnCl₃⁻, SbF₃OH⁻, AsF₃⁻, and SbO₂⁻.
 The curium agent can be present in the range of 0.1 to 20, preferably 0.1 to 10 weight percent of the total composition. The ratio of organometallic compound to curium salt is in the range of 10:1 to 1:10 by weight.

The present invention also provides a process for the polymerization of ethylenically-unsaturated monomers in combination with one of polyurethane precursors and epoxy monomers comprising the steps

- (a) providing a mixture of at least one ethylenically-unsaturated monomers and either poly urethane precursors or an epoxy compound;

- (b) adding to said mixture a combination of a catalytically effective amount comprising an organometallic compound and an curium salt (and all parameters of the aforementioned components), thereby forming a polymerizable mixture, and
 (c) allowing the mixture to polymerize or adding energy to the mixture to effect polymerization in a further aspect, there is also provided a method for preparing coated articles of composition of the invention comprising the steps of

- (a) providing a substrate;
 (b) coating an energy polymerizable mixture as described above to the substrate in the art, such as bar, knife, reverse roll, laminated roll or spin coating, or by dipping and the like, with or without a coating solvent, and
 (c) applying energy (after evaporation or solvent if present) to the article to cause the curing.

In a still further aspect, there are also provided shaped articles comprising the polymer of the invention. The articles can be provided, for example, by techniques such as molding, casting, and extrusion. Applying energy to the mixture causes polymerization and shaped article.

It is not preferred, but it may be desirable to add solvent to solubilize the processing. Solvent, preferably an organic solvent in an amount up to 50 weight percent, the range of 0 to 50 weight percent, most preferably in the range of 10 to 75 weight percent, polymerizable composition can be used.

There are restrictions on the total sum of electrons donated by the ligands L₁, L₂, and L₃ to the metal M. For most organometallic compounds the valence electrons possessed by the metal M are given by the "valence electron rule" (VER) which states that the sum of the valence electrons of the metal M and the valence electrons of the ligands L₁, L₂, and L₃ must equal the "magic number" 2, 10, 18, 36, 54, 72, 90, 118, 138, 154, 182, 210, 228, 258, 286, 314, 342, 370, 398, 426, 454, 482, 510, 538, 566, 594, 622, 650, 678, 706, 734, 762, 790, 818, 846, 874, 902, 930, 958, 986, 1014, 1042, 1070, 1098, 1126, 1154, 1182, 1210, 1238, 1266, 1294, 1322, 1350, 1378, 1406, 1434, 1462, 1490, 1518, 1546, 1574, 1602, 1630, 1658, 1686, 1714, 1742, 1770, 1798, 1826, 1854, 1882, 1910, 1938, 1966, 1994, 2022, 2050, 2078, 2106, 2134, 2162, 2190, 2218, 2246, 2274, 2302, 2330, 2358, 2386, 2414, 2442, 2470, 2498, 2526, 2554, 2582, 2610, 2638, 2666, 2694, 2722, 2750, 2778, 2806, 2834, 2862, 2890, 2918, 2946, 2974, 3002, 3030, 3058, 3086, 3114, 3142, 3170, 3198, 3226, 3254, 3282, 3310, 3338, 3366, 3394, 3422, 3450, 3478, 3506, 3534, 3562, 3590, 3618, 3646, 3674, 3702, 3730, 3758, 3786, 3814, 3842, 3870, 3898, 3926, 3954, 3982, 4010, 4038, 4066, 4094, 4122, 4150, 4178, 4206, 4234, 4262, 4290, 4318, 4346, 4374, 4402, 4430, 4458, 4486, 4514, 4542, 4570, 4598, 4626, 4654, 4682, 4710, 4738, 4766, 4794, 4822, 4850, 4878, 4906, 4934, 4962, 4990, 5018, 5046, 5074, 5102, 5130, 5158, 5186, 5214, 5242, 5270, 5298, 5326, 5354, 5382, 5410, 5438, 5466, 5494, 5522, 5550, 5578, 5606, 5634, 5662, 5690, 5718, 5746, 5774, 5802, 5830, 5858, 5886, 5914, 5942, 5970, 6000, 6028, 6056, 6084, 6112, 6140, 6168, 6196, 6224, 6252, 6280, 6308, 6336, 6364, 6392, 6420, 6448, 6476, 6504, 6532, 6560, 6588, 6616, 6644, 6672, 6700, 6728, 6756, 6784, 6812, 6840, 6868, 6896, 6924, 6952, 6980, 7008, 7036, 7064, 7092, 7120, 7148, 7176, 7204, 7232, 7260, 7288, 7316, 7344, 7372, 7400, 7428, 7456, 7484, 7512, 7540, 7568, 7596, 7624, 7652, 7680, 7708, 7736, 7764, 7792, 7820, 7848, 7876, 7904, 7932, 7960, 7988, 8016, 8044, 8072, 8100, 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24392, 24420, 24448, 24476, 24504, 24532, 24560, 24588, 24616, 24644, 24672, 24700, 24728, 24756, 24784, 24812, 24840, 24868, 24896, 24924, 24952, 24980, 25008, 25036, 25064, 25092, 25120, 25148, 25176, 25204, 25232, 25260, 25288, 25316, 25344, 25372, 25400, 25428, 25456, 25484, 25512, 25540, 25568, 25596, 25624, 25652, 25680, 25708, 25736, 25764, 25792, 25820, 25848, 25876, 25904, 25932, 25960, 25988, 26016, 26044, 26072, 26100, 26128, 26156, 26184, 26212, 26240, 26268, 26296, 26324, 26352, 26380, 26408, 26436, 26464, 26492, 26520, 26548, 26576, 26604, 26632, 26660, 26688, 26716, 26744, 26772, 26800, 26828, 26856, 26884, 26912, 26940, 26968, 26996, 27024, 27052, 27080, 27108, 27136, 27164, 27192, 27220, 27248, 27276, 27304, 27332, 27360, 27388, 27416, 27444, 27472, 27500, 27528, 27556, 27584, 27612, 27640, 27668, 27696, 27724, 27752, 27780, 27808, 27836, 27864, 27892, 27920, 27948, 27976, 28004, 28032, 28060, 28088, 28116, 28144, 28172, 28200, 28228, 28256, 28284, 28312, 28340, 28368, 28396, 28424, 28452, 28480, 28508, 28536, 28564, 28592, 28620, 28648, 28676, 28704, 28732, 28760, 28788, 28816, 28844, 28872, 28900, 28928, 28956, 28984, 29012, 29040, 29068, 29096, 29124, 29152, 29180, 29208, 29236, 29264, 29292, 29320, 29348, 29376, 29404, 29432, 29460, 29488, 29516, 29544, 29572, 29600, 29628, 29656, 29684, 29712, 29740, 29768, 29796, 29824, 29852, 29880, 29908, 29936, 29964, 29992, 30020, 30048, 30076, 30104, 30132, 30160, 30188, 30216, 30244, 30272, 30300, 30328, 30356, 30384, 30412, 30440, 30468, 30496, 30524, 30552, 30580, 30608, 30636, 30664, 30692, 30720, 30748, 30776, 30804, 30832, 30860, 30888, 30916, 30944, 30972, 31000, 31028, 31056, 31084, 31112, 31140, 31168, 31196, 31224, 31252, 31280, 31308, 31336, 31364, 31392, 31420, 31448, 31476, 31504, 31532, 31560, 31588, 31616, 31644, 31672, 31700, 31728, 31756, 31784, 31812, 31840, 31868, 31896, 31924, 31952, 31980, 32008, 32036, 32064, 32092, 32120, 32148, 32176, 32204, 32232, 32260, 32288, 32316, 32344, 32372, 32400, 32428, 32456, 32484, 32512, 32540, 32568, 32596, 32624, 32652, 32680, 32708, 32736, 32764, 32792, 32820, 32848, 32876, 32904, 32932, 32960, 32988, 33016, 33044, 33072, 33100, 33128, 33156, 33184, 33212, 33240, 33268, 33296, 33324, 33352, 33380, 33408, 33436, 33464, 33492, 33520, 33548, 33576, 33604, 33632, 33660, 33688, 33716, 33744, 33772, 33800, 33828, 33856, 33884, 33912, 33940, 33968, 33996, 34024, 34052, 34080, 34108, 34136, 34164, 34192, 34220, 34248, 34276, 34304, 34332, 34360, 34388, 34416, 34444, 34472, 34500, 34528, 34556, 34584, 34612, 34640, 34668, 34696, 34724, 34752, 34780, 34808, 34836, 34864, 34892, 34920, 34948, 34976, 35004, 35032, 35060, 35088, 35116, 35144, 35172, 35200, 35228, 35256, 35284, 35312, 35340, 35368, 35396, 35424, 35452, 35480, 35508, 35536, 35564, 35592, 35620, 35648, 35676, 35704, 35732, 35760, 35788, 35816, 35844, 35872, 35900, 35928, 35956, 35984, 36012, 36040, 36068, 36096, 36124, 36152, 36180, 36208, 36236, 36264, 36292, 36320, 36348, 36376, 36404, 36432, 36460, 36488, 36516, 36544, 36572, 36600, 36628, 36656, 36684, 36712, 36740, 36768, 36796, 36824, 36852, 36880, 36908, 36936, 36964, 36992, 37020, 37048, 37076, 37104, 37132, 37160, 37188, 37216, 37244, 37272, 37300, 37328, 37356, 37384, 37412, 37440, 37468, 37496, 37524, 37552, 37580, 37608, 37636, 37664, 37692, 37720, 37748, 37776, 37804, 37832, 37860, 37888, 37916, 37944, 37972, 38000, 38028, 38056, 38084, 38112, 38140, 38168, 38196, 38224, 38252, 38280, 38308, 38336, 38364, 38392, 38420, 38448, 38476, 38504, 38532, 38560, 38588, 38616, 38644, 38672, 38700, 38728, 38756, 38784, 38812, 38840, 38868, 38896, 38924, 38952, 38980, 39008, 39036, 39064, 39092, 39120, 39148, 39176, 39204, 39232, 39260, 39288, 39316, 39344, 39372, 39400, 39428, 39456, 39484, 39512, 39540, 39568, 39596, 39624, 39652, 39680, 39708, 39736, 39764, 39792, 39820, 39848, 39876, 39904, 39932, 39960, 39988, 40016, 40044, 40072, 40100, 40128, 40156, 40184, 40212, 40240, 40268, 40296, 40324, 40352, 40380, 40408, 40436, 40464, 40492, 40520, 40548, 40576, 40604, 40632, 40660, 40688, 40716, 40744, 40772, 40800, 40828, 40856, 40884, 40912, 40940, 40968, 40996, 41024, 41052, 41080, 41108, 41136, 41164, 41192, 41220

active groups
and
the polymerizable group, via

either polymerizable com-
ponents and 1 to
the polymerizable group, via
and a polymerizable group

at: at the same or different ligand
calculated compounds and groups and
atomic compounds each capable of
different containing an even number of
each containing 2, 4 or 6 sigma electrons
different each contributing no more than
from the elements of Periodic Groups
metals
at least one of a metal-metal sigma bond and
at least one a stable configuration, and

Patent Nos. 3,708,286; 3,729,313; 3,741,769;
4,111,513; 4,216,288; 4,394,403 and 4,623,676.
wherein where more preferably A is selected
from: Quaternarybutyltin and
those in which A is an organic sulfonate or
in which SO₂ - p-chlorophenyl p-chloroben-

Groups 1B to VIIIb or a metal or metallo
a larger atom and is an integer having a
aluminum chromium manganese iron
antimony in a zinc and Pb, Fe,
etc. Preferably the atoms are
valency 1 to 10 weight percent of the
all is in the range of 10 to 110 by

of ethylenically unsaturated
monomers undergoing the steps
of polymerization and either polymerizable

(b) adding to said mixture a combination of a catalytically effective amount of a curing agent
comprising an organometallic compound and an onium salt (and all permutations of the order of mixing the
above-mentioned components), thereby forming a polymerizable mixture, and

(c) allowing the mixture to polymerize or adding energy to the mixture to effect polymerization
In a further aspect, there is also provided a method for preparing coated articles containing the cured
composition of the invention comprising the steps of:

(a) providing a substrate
(b) coating an energy polymerizable mixture as described above to the substrate by methods known
in the art, such as bar, knife, reverse roll, inverted roll, or spin coatings, or by dipping, spraying, brushing,
and the like, with or without a coating solvent, and
(c) applying energy (after evaporation of solvent, if present) to the article to cause the polymerization
of the coating

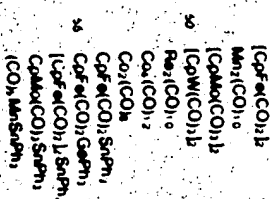
In a still further aspect, there are also provided shaped articles comprising the polymerizable mixture of
the invention. The articles can be provided, for example, by techniques such as molding, injection molding,
casting, and extrusion. Applying energy to the mixture causes polymerization and provides the cured
shaped article.

It is not preferred, but it may be desirable to add solvent to solidify components and aid in
processing. Solvent, preferably an organic solvent in an amount up to 99 weight percent, but preferably in
the range of 0 to 90 weight percent, most preferably in the range of 0 to 75 weight percent, of the
polymerizable composition can be used.

There are restrictions on the total sum of electrons donated by the ligands, L₁, L₂, L₃ of formula I and
the valence electrons possessed by the metal. For most organometallic compounds not involving in-
tramolecular metal-metal bonding, this sum is governed by the "eighteen electron rule" [see J. Chem. Ed.
46, 811 (1969)]. This rule is sometimes called the "magic number rule". The effective number rule, or the
"five gas rule". This rule states that the most stable organometallic compounds tend to be those
compounds in which the sum of the electrons donated by the ligands and the metal is eighteen. Those
skilled in the art, however, know that there are exceptions to this rule and that organometallic compounds
having a sum of 16, 17, 19, and 20 electrons, are also known. Therefore, organometallic compounds not
including intramolecular metal-metal bonding are described by formula I, in which completed metals having
a total sum of 16, 17, 18, 19, or 20 electrons in the valence shell are included within the scope of the
invention.

For compounds described in formula I in which intramolecular metal-metal bonding exists serious
departure from the "eighteen electron rule" can occur. It has been proposed [J. Amer. Chem. Soc. 100,
5305 (1978)] that the departure from the "eighteen electron rule" in these transition metal compounds is
due to the metal-metal interactions destabilizing the metal p orbitals to an extent to cause them to be
unavailable for ligand bonding. Hence, rather than count electrons around each metal separately in a metal
cluster, cluster valence electrons (CVE) are counted. A dinuclear compound, having tetrahedral, butterfly, and square
planar geometry is seen to have 80, 82, or 84 CVEs, respectively. Those skilled in the art, however, know
that there are exceptions to this electron counting method and that organometallic complex cluster
compounds having a sum of 42, 44, 46, 50 CVEs for a trinuclear compound and 58 CVEs for a tetranuclear
compound are also known. Therefore, di, tri, or tetranuclear organometallic compounds are described by
formula I in which the completed metal cluster, M₁M₂M₃ or M₁M₂M₃M₄ has a total sum of 34, 42, 44, 46, 48,
50, or 58, 60, 62, 64 CVEs in the valence shell, respectively, and are included within the scope of this
invention.

Illustrative examples of organometallic compounds according to formula I include:



in which: 1 is nitrogen; 2 to 4, and Q represents an aliphatic hydrocarbon di-, tri-, or tetra-radical containing from 2 to 4 carbon atoms, and zero to 50 heteroatoms; a cycloaliphatic hydrocarbon radical containing from 2 to 4 carbon atoms and zero to 50 heteroatoms; an aromatic hydrocarbon radical or heterocyclic from 4 to 100 carbon atoms and zero to 50 heteroatoms; an aromatic hydrocarbon radical or heterocyclic aromatic radical containing from 5 to 15 carbon atoms and zero to 10 heteroatoms; or an arylphosphorus heteroatom radical containing from 6 to 100 carbon atoms and zero to 50 heteroatoms. The heteroatoms may be hydrocarbon radical containing from 6 to 100 carbon atoms and zero to 50 heteroatoms, nitrogen, silicon, and that can be present in Q include non-peroxide oxygen, sulfur, non-amino nitrogen, halogen, silicon, and non-phosphorus phosphorus.

Examples of polyisocyanate

Examples of polyisocyanates are as follows:

20. *n*-hexamethylene diisocyanate, 1,6-hexamethylene diisocyanate, trimethyl hexamethylene diisocyanate, 1,4-tetramethylene diisocyanate, cyclobutane-1,3-diol-1,4-diisocyanate, 1,12-dodecane diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3- and 1,4-diisocyanate and mixtures of these isomers, 1-isocyanato-3,5-timethyl-5-isocyanatomethyl cyclohexane (see German Auslegeschrift No. 1,702,785, U.S. Patent No. 3,401,180), 2,4- and 2,6-hexyldiololene diisocyanate and mixtures of these isomers, hexadecyl-1,3- and/or -1,4-phenylene diisocyanate, perfluoro-diisocyanate and mixtures of these isomers, hexadecyl-2,4- and/or -2,6-hexane diisocyanate and mixtures of these isomers, hexadecyl-1,3- and/or -1,4-phenylene diisocyanate, 2,4- and 2,6-hexane diisocyanate and mixtures of these isomers, diphenyldiurea-2,4- and/or -4,4'-diisocyanate, neopentylster-1,5-diisocyanate, and the reaction products of four equivalents of the aforementioned isocyanate-containing compounds with compounds containing two isocyanate-reactive groups

compounds with continuous conjugation it is also possible for example, to use triphenyl methylene-4,4',4''

According to the present invention, the above-mentioned polyisocyanates described in British Patent Nos. 874,430 and 868,871, m- and p-secyanophenyl sulphonyl isocyanates according to U.S. Patent No. 3,454,808, perfluorinated aryl polyisocyanates of the type described, for example, in German Auslegeschrift No. 1,157,601 (U.S. Pat. No. 3,277,138), polyisocyanates containing carbodiimide groups of the type described, in U.S. Patent No. 3,152,162 and in German Offenlegungsschrift Nos. 2,504,400, 2,537,685 and 2,552,350, in German Patent No. 3,482,330, polyisocyanates containing chelate groups of the type described, for example, in British Patent No. 964,880, in Belgian Pat. No. 781,828 and in groups of the type described, for example, in British Patent No. 964,880, in Belgian Patent No. 781,828 and in German Offenlegungsschrift Nos. 1,928,034 and 2,004,046, polyisocyanates containing isocyanate groups of the type described, for example, in U.S. Patent No. 3,001,873, in German Patent Nos. 1,022,769, 1,222,067 and 1,027,364 and German Offenlegungsschrift Nos. 1,928,034 and 2,004,046, polyisocyanates containing urea groups of the type described, for example, in Belgian Patent No. 792,281 or in U.S. Patent Nos. 3,364,164 and 3,464,457, polyisocyanates containing thioether groups of the type described, for example, in U.S. Patent No. 1,230,778, polyisocyanates containing thioether groups of the type described, for example, in U.S. Patent No. 1,234,605, 3,280,372 and 3,124,605 and in British Patent No. 683,050, polyisocyanates produced by isocyanate reactions of the type described, for example, in U.S. Patent No. 3,664,102, polyisocyanates containing urethane groups of the type described, for example, in British Patent Nos. 636,474 and 1,072,656, in German Patent No. 3,567,703 and in German Patent No. 1,231,652, reaction products of the above-mentioned diisocyanates with addenda according to German Patent 1,072,385 and polyisocyanates containing polymeric diisocyanates such as those according to U.S. Patent No. 3,456,623.

It is also possible to use dextran isolated having 100,000 g/mol obtained in the commercial production of 100,000, especially in solution in one or more of the above-mentioned polyols, and to produce in this way new variants of the dextran-encapsulated polyol systems.

[illegible]

Lee and Nienke, McGraw Hill Book Company, New York (1967) and in "Epoxy Resin Technology" by P. F. Burns, John Wiley & Sons, New York (1968). Representative of the 1,3- and 1,4-cyclic ethers which can be polymerized in accordance with this invention are oxetane, 3,3-bis(chloromethyl)oxetane, and epichlorohydrin.

[illegible][illegible]

amides such as nadic, methyl acrylate, cyclopentanone, and mixtures thereof.

As noted above, the organometallic compounds useful in the curing agents useful in the invention have the formula

Ligands L to L' are well known in the art of transition metal organometallic chemistry. Ligand L' of general formula I is provided by any monomeric or polymeric compound having accessible unsaturated group, i.e., an ethynyl, $-C\equiv C-$ group, acetylenic, $-C\equiv C-$ group, or aromatic group which has accessible π -electrons regardless of the total molecular weight of the compound.

[illegible][illegible][illegible][illegible][illegible]

As mentioned before the ligand can be a unit of a polymer, in other words poly(styrene-co-butadiene), poly(styrene-co-methyl methacrylate), polystyrene, poly(styrene-co-butadiene), poly(styrene-co-methyl methacrylate), poly(vinylcarbazole) and polymethacrylates; the cyclopentadiene group in poly(vinylcyclopentadiene).

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[illegible][illegible]

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[illegible]

ununsaturated group and the metal atom. By polymeric compounds having less than 60 carbon atoms, and from 280 to 10 hetero atoms selected from boron, phosphorus, arsenic, selenium, tellurium, antimony, bismuth, lead, tin, germanium, silicon, sulfur, oxygen, nitrogen, fluorine, chlorine, bromine, iodine, and hydrogen.

[illegible][illegible][illegible]

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the pyridine group in poly(vinylpyridine), etc. Polymers having a weight average molecular weight up to 100,000 can be used. It is preferable that 5 to 50 percent of the unsaturated or aromatic groups be composed with metallic cations.

[illegible][illegible][illegible]

proposed that only one election is allowed per year.

M can be separated from the Periodic Groups Nb, Vb, Vc, Mo, W, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Hf, Ta, Pb and Pt.

Zi, M. V. MD, T. C. C. MD, W. M. T. C. MD, F. G. MD, U. C. MD, V. C. MD, and J. C. MD.

in general, radiation-induced polymerization is carried out with latent curing agents comprising an organotin compound in a suitable composition.

these precursors and epoxy resins are used for the majority of energy storage and an ocean salt can be carried out at room temperature for the majority of energy storage.

[illegible][illegible][illegible][illegible][illegible][illegible]

[illegible][illegible][illegible]

...and use of isolated
...metallic compounds
...and compounds

amount low temperature (e.g., -10°C) or elevated temperature (e.g., 30 to 200°C, preferably 50 to 150°C) can be used to subdue the asbrom of polymerization or to accelerate the polymerization, respectively. Temperature of polymerization and amount of catalyst will vary and be dependent on the particular curable composition used and the desired application of the polymerized or cured product. The amount of curing agent to be used in this invention should be sufficient to effect polymerization of the polymerizable mixtures (i.e., a catalytically-effective amount) under the desired use conditions. Such amount generally will be in the range of about 0.1 to 20 weight percent, and preferably 0.1 to 10.0 weight percent based on the weight of curable composition.

While not arising to be bound by theory, we propose that when species intermediate compounds are irradiated in the presence of suitable oxidizing agents such as oxium salts, urethanes and vinyl monomers, it is believed that the produced which can affect the curing of epoxides, urethanes and vinyl monomers. It is believed that the transition metal-transition metal or metal- π sigma bond cleaves homolytically upon photolysis. Evidence for this homolytic cleavage is provided for some organometallic compounds such as $[\text{Co}(\text{Cp})(\text{Cl})_2]$ and $\text{Mn}(\text{CO})_5$ and involves the abstraction of Cl from CCl_4 subsequent to photolysis (G. Goettley and M. Wrighton, "Organometallic Photochemistry," Academic Press, NY (1979), Chapters 2 and 8, particularly p. 138) in other cases, spectroscopic data provides such evidence (O. Haeberle, A. Wojcicki Angew. Chem. 1983, 44, 163; R. G. Severson, A. Wojcicki, J. Organomet. Chem. 1978, 157, 173). The products of this bond homolysis then react with the oxidizing agent. By this process, the catalytic species for the polymerization of either the polyurethane precursors or epoxy monomers is derived from the organometallic compound and, simultaneously the free radical initiator for the polymerization of the ethylenically unsaturated monomers is derived from the oxidizing agent. In the limit, cleavage of the sigma bond by one photon can ultimately lead to the production of two organometallic-derived species and two free radical initiators. It should be noted that competing or secondary photo processes, such as dissociation of a carbonyl ligand, can occur. Such processes, however, occur in such a manner or to such an extent that the effective

Solvents, preferably organic can be used to assist in dissolution of the curing agent in the epoxy resin and as a processing aid. Representative solvents include acetone, methyl ethyl ketone, cyclopentanone, methyl cellosolve acetate, methylene chloride, nitromethane, methyl formate, acetonitrile, gamma-butyrolactone, and 1,2-dimethoxyethane (DME) in some applications. It may be advantageous to add the curing agent onto an inert diluent (DME) in some applications. U.S. Patent No. 4,677,137

For those compositions of the invention which are radiation-sensitive, i.e., the compositions containing support such as silica, alumina, clays, etc., as described in U.S. Pat. No. 3,706,897, the compositions containing ethylenically unsaturated monomers and either polyurethane precursors or epoxy monomers and/or curing agent a combination of an organometallic compound of Formula I and an oxum salt of Formula II, any source of radiation including electron beam radiation and radiation sources emitting active radiation in the ultraviolet and visible regions of the spectrum (e.g., about 200 to 800 nm) can be used. Suitable sources of radiation include mercury vapor discharge lamps, carbon arc, tungsten lamps, xenon laser, lasers, ultraviolet and visible region of the spectrum (e.g., about 200 to 800 nm) can be used. Suitable sources of radiation include mercury vapor discharge lamps, carbon arc, tungsten lamps, xenon laser, lasers, ultraviolet and visible region of the spectrum (e.g., about 200 to 800 nm) can be used. Suitable sources of radiation include mercury vapor discharge lamps, carbon arc, tungsten lamps, xenon laser, lasers, ultraviolet and visible region of the spectrum (e.g., about 200 to 800 nm) can be used.

The required amount of exposure to effect polymerization is dependent upon such factors as the identity and concentrations of the organometallic compound and oxum salt, the particular ethylenically unsaturated monomer, polyurethane precursors, and epoxy monomers; the thickness of the exposed surface of the substrate; intensity of the radiation source and amount of heat associated with the

Thermal polymerization using direct heating or infrared electromagnetic radiation, as is known in the art, can be used to cure ethylenically-unsaturated monomers and other polyurethane pre-cursors or copoly-
mers by first activating the monomers with the

monomers according to the two-stage polymerization (curing) by the irradiation. It is within the scope of the present invention to cure the activated curing agent by irradiating the curable compositions and subsequently thermally curing the polymerized compositions. The irradiation temperatures being below the temperatures employed for the subsequent curing. These activated precursors may normally be cured at temperatures in the range from 50 to 150°C. This two-stage curing, with an advantage in the range from 50 to 110°C. This two-stage curing also makes it possible to control the polymerization in a particularly simple and advantageous manner.

[illegible]

ENERGY-INDUCED DUAL CURABLE UHMW

FIELD OF THE INVENTION

This invention relates to an energy-polymerizable compound and other polymerizable structures or an energy-monomer and other polymerizable compound and an oxidizing agent and to an organometallic compound and a catalyst and to articles comprising the composition of the invention as, for example, as protective coatings, binders for magnetic media applications.

Background Of The Invention

Various polymeric coatings and adhesives are being developed for use in 1983-84 solvents. There is an intense effort by law enforcement agencies to reduce the use of such solvents in formulations to reduce or eliminate the use of such solvents. These processes require a total contamination. These processes are activated in a controlled fashion.

Thermal Curing of Polyurethane Prepolymers
Baranmes is known in the art Curing of Polymerization
to as polyurethane precursors) using thermally stable
Cured Nos. 4521 945 and 4582 8611

Producing of urethane (methacrylates) is well known. Patent 2,620,000 (1953) describes the reaction of an isocyanate with a polyurethane. S. Y. Tsay, M. Koshida, Y. S. Ding, S. L. Cooper, & J. Polym. Plast. Technol. Eng. 1981, 17, 83-93, and patent.

The dual curing of acrylates with urethane precur-

entirely photoreactive for the synthesis of polymers. The photoreactive precursors and activators (see U.S. Pat. 4,342,93; pages 46-55)

[illegible]

which the polymerization catalyst is a radical initiator, as described in U.S. Patent No. 3,764,576 and U.S. Patent No. 4,028,705 and the known state of the art.

⁶⁶ U.S. Patent No. 4,216,788 teaches the thermal im-

onium salts and reducing agents.
Reaction with curable compositions containing eth-
oxymers have been described in U.S. Patent Nos. 4,156,111
50 include onium salts combined with organic carbonates,
organosilicon compounds.

Energy polyimide compositions (company "cathodically sensitive materials and the curing thereof")
Nos. 108 051, 1204 Derwent abstract, 084 915 1965
abstract)

Many examples of the
different motions and
the various ways in which
the motion of the water
is affected by the motion
of the vessel and the
wind.

[illegible]

10-15
20-100
40-100
4-100

These compounds are used in subsequent examples.

54

11/11/2010

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1

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100-443887-100

Conclusion:

Order No.	5	1
Quantity	1	1

However, the curing agent composition

100

NR, VR, VED, VMD, and VMD (continued) : 2000

2. In certain cases, consideration may be given to the

1

not rejected from 1900-1950.

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CRIMINAL RECORDS

RECURSOS DE INFORMACIÓN

EXAMPLE 6 (Comparative)

This example illustrates the photocuring of polyurethane precursors to polyurethanes in the presence of a photoinitiator. The photoinitiator used is a benzoin derivative, benzoin ethyl ether, which is a common salt as curing agent.

Ornam salt as curing agent. A mixture of 10 mg [$\text{Cp}^*\text{Fe}(\text{CO})\text{H}$], 30 mg Ph_3I , pf_6^- , 0.1 g gamma-butyrolactone, 0.63 g Desmodorin salt as curing agent, and 1.17 g polyethyleneglycol (MW = 400) was divided in two glass ampoules. One ampoule was bubbled with N_2 for 2-3 minutes, the other left open to the atmosphere. Both samples were irradiated simultaneously with the output of a 460 watt Harrow mercury lamp, filtered through Pyrex. The ampoules were retrieved after 100 minutes irradiation. This demonstrates that in the presence of ornam salt, curing occurs with or without O_2 present.

EXAMPLE 7 (Comparative)

This example describes the photocuring of polyurethane precursors using transition metal containing organometallic compounds and lithium and sodium salts. A stock solution was prepared from 7 parts Deminor[®] W, 1.9 parts butanediol, and 0.5 parts trimethylolpropane. Samples were prepared as in Example 20 using 1.25 g of the stock solution, 0.01 g neutral metal-metal bonded compound and 0.015 g Ph⁺PF₆⁻ in 0.05 g gamma-butyrolactone. Inclusions were carried out on a 450 W Hanovia medium pressure mercury arc through Pyrex. Alternatively, these compositions can be cured thermally.

TABLE II

Isotarium and Sulfonium Salts		
Organometallic Compound	Cure time, minutes	
	Ph ₁ ⁺ PF ₆ ⁻	Ph ₂ S ⁺ PF ₆ ⁻
[Cat(CO) ₂] ₂	6.0	>100
[CpFe(CO) ₂] ₂	9.0	20-25
[Mn(CO) ₅] ₂	12-20	7-12
[Ru(CO) ₃] ₂	20-40	20-40
Co ₂ (CO) ₈	40-55	55-66
[CpCo(CO) ₂] ₂	55-67	60-70
Fe ₂ (CO) ₉	ca. 60	—

EXAMPLE 8 (Comparative)

This provides further examples of biocomponent curing agents wherein organometallic compounds A contain various metal-carbon bonds which are effective in the curing agent for polyurethane precursors. A certain variation metal-carbon bonds which are effective in the curing agent for polyurethane precursors. A certain variation metal-carbon bonds which are effective in the curing agent for polyurethane precursors.

30 stock solution of polyurethane precursors was prepared by mixing 23.1 g Dabondur W and 32.8 g Carbonox 400 and stirring well before use. Samples were prepared by dissolving 10 mg catalyst and 20 mg diisocyanate in the stock solution. The temperature of samples was then irradiated under a Hemoval Quartz Uv Lamp. The time to a viscosity increase is noted in Table III, and "Cure time" is the time for a sample to become so viscous that it would not flow. "Partial Cure" is indicated when, within 30 min irradiation, the sample became more viscous but would still flow.

TABLE III

Curing of Polyurethane Precursors		
	Cure Rates, min	
	Viscosity Increase	Cured
CapPhtes:	7	30
CapPhtes + isodorum	7	30
CapW(CO) ₂ Me	30	partial
CapW(CO) ₂ Me + isodorum	30	partial
[(Phtes), Ph ₂ Phtes](acetone)] + PF ₂ -	13	partial
[CapW(CO) ₂ Me + isodorum] ^a	9	partial
		30

2 included for purposes of comparison

The data show curing occurs with or without roddmann salts. In some cases, adenosine 3'-VG provides a suitable oxidizing agent. However, the use of uracil salts is preferred since it is much easier to control the organometallic oxidizing agent (280).

EXAMPLE 9 (Comparative)

This example describes the use of the curing agent containing an organosilastic compound (I) as a transition metal-carbon bond to cure epoxides. Each sample was prepared by dissolving 10 mg of a transition metal-carbon bond reagent (II) in 0.2 g CH₂Cl₂, 2.0 g cyclohexanone, 1.0 g triethylamine, and 20 mg diphenyliodonium hexafluorophosphate (if used) in 0.2 g CH₂Cl₂. The mixture was added in the dark, and samples were then irradiated under a Hanovia Quartz lamp (model I-1). The polymer was tested by placing a few drops of the sample in about 2 mL methanol. Formation of a precipitate indicated that polymer had formed. Further polymerization resulted in a viscosity increase in "Results are indicated in Table IV."

TABLE N

Curing Agent	Precipitate formed, mm	Viscosity increased, mm.
CapPals [®]	no cure	no cure
CapPals [®] + iodourum	3.5	
CapW(CO ₂ H) + iodourum	3	
(Pals [®] ; Ph ₂ Pals [®] ; (acetonals)) + Ph ₂ ^a	2	no further cure
[CapW(CO ₂ H) + iodourum] ^b	2	30

2 included for purposes of comparison

EXAMPLE 10 (Comparative)

[illegible]

ded to prepare the coating solution. The solutions were coated onto 76 micrometers (3 mil) polyvinylidene chloride sanded polyester (3M Company) using a #22 wire wound rod. The sample coatings were exposed in air to a 275 watt G.E. sunlamp at a distance of 10 cm. The time to "set to cotton" is recorded in Table V. It is the time needed to cure the coating so that when it is touched with a cotton ball it leaves no smears. This test establishes the time required to cure the coating. Under the conditions of this test the diphenylidonium hexafluorophosphate alone requires greater than 10 min. to cure.

TABLE V

Photocrosslinking of Epoxy Cure		
Compound	Cure Time*	
	No Onium Salt Added	Onium Salt Added
[CpFe(CO) ₂ Li]	>10	1
[CpFe(CO) ₂ SnPh ₃]	>10	5
[CpFe(CO) ₂ GePh ₃]	>10	5
[CpFe(CO) ₂ Li]SnPh ₃	>10	3
Me ₃ (CO) ₃	>10	1
(CO) ₂ MeSnPh ₃	>10	4
(tCCl ₃) ₂ MeLiSnPh ₃	>10	3
Ph ₃ C(CO) ₂ Li	1	15
Cp*Fe(CO) ₂ Li	8	4

EXAMPLE 11 Comparative

To further demonstrate the activity of the curing agent, a series of experiments were carried out in which epoxy and/or acrylate composition. The organometallic compound with and without the crown salt was polymerized in presence of an epoxy or acrylate. The specific system used is as follows: methyl acrylate was distilled from hydronone and stored (and until ready for use) Cyclohexene oxide was used as obtained from Aldrich. The organometallic compounds were obtained from commercial sources. Diphenylphosphonium tetrafluoroborate was recrystallized from acetone isopropanol. All experiments were done at 100°C. Solids are listed as noted.

In a small vial was placed 0.02 g of the organometallic compound with without 0.14 g of the monomer (in a small vial) was placed 0.02 g of the organometallic compound with without 0.14 g of the monomer. For the acrylate tests the solutions were purged with N_2 for 60 min. The epoxy tests were performed without purging. The curing tests were performed with the crown salt being added continuously during the polymerization. The epoxy tests were performed without the crown salt being added continuously during the polymerization. The curing tests were performed with the crown salt being added continuously during the polymerization. The curing tests were performed with the crown salt being added continuously during the polymerization.

Produced Cure Times of Epoxies and Acrylate Composites ^a		
Catalyst System	Epoxies	Acrylate
[Cp ⁺ Et(CO ₂ Cl)] _b	~900	~600
[Cp ⁺ Et(CO ₂ Cl)] _b	80	10
Allyl ₂ (CO ₂) ₂	~900	~600
Allyl ₂ (CO ₂) ₂	200	45
Ph ₂ (CO ₂) ₂	~900	~90
Ph ₂ (CO ₂) ₂	200	90
Co ₂ (CO) ₈	1000000	10
Co ₂ (CO) ₈	1000000	200
Co ₂ (CO) ₈	1000000	10
Co ₂ (CO) ₈	1000000	10
Co ₂ (CO) ₈	1000000	100

TABLE VI

14. This aromatic demonstrates the ability of halogenated aromatic compounds to act as gamma-emitting compounds to photoinitiate the cure of ultraviolet-curable inks at a dosage of sodium salts. The tests were carried out in the following sequence: into a glass of sodium salts. The tests were carried out in the following sequence: into a glass of sodium salts. The tests were carried out in the following sequence: into a glass of sodium salts.
15. Company (recrystallized from acetone reprecipitation). Then the following procedure: 0.05g of the desired organometallic compound and a 10g of sodium acetate. The tests were carried out in the following sequence: into a glass of sodium salts. The tests were carried out in the following sequence: into a glass of sodium salts.

EXAMPLE 12 (continued)

11

TABLE VI

Photoinitiated Cure Times of Epoxy and Acrylic Compositions ^a		
Catalyst System	Epoxy	Acrylic
[CpFe(CO) ₂ h] iodonium	> 800 80	> 800 30
[CpFe(CO) ₂ h] iodonium	> 800 200	> 800 45
Re ₂ (CO) ₉ : iodonium	> 800 200	380 60
Re ₂ (CO) ₉ : iodonium	b	b
Co ₂ (CO) ₈ : iodonium	c	200
Co ₂ (CO) ₈ : iodonium	d	d
Ca(CO) ₂ : iodonium ^d	> 800 > 800	80 > 300

^a Cure time in seconds^b Not done^c Reacted in the dark upon mixing^d 10% by wt gamma-butyrolactone added

EXAMPLE 12 (Cumulative)

This example demonstrates the ability of transition metal-uranium model bonded or ML₂ type or organometallic compounds to photoinitiate the cure of ethylenically unsaturated compounds in the presence of adductum salts. The tests were carried out in the following manner: Into a glass vial were weighed out 0.05g of the desired organometallic compound and/or 0.10g diethylenetriamine hexafluorophosphate (25) 0.05g of the desired organometallic compound. Then the following operations were carried out under subdued light: 0.2g of gamma-butyrolactone (50g methyl acrylate (Aldrich Chemical Company, distilled from hydrazine), 5.0g of pentaerythritol tetracrylate (SA-285, Sartomer Company) were added to produce the coating solution. The solutions were coated onto 76 micrometer (3 mil) polyethylene sheets, the coated polyester (25) Company) using a #22 wire wound rod. The sheets were exposed at a distance of 2 cm. The second sheet of polyester and exposed to two 15 watt Sytona ultraviolet bulbs at a distance of 2 cm. The time required to produce a non-tacky cured coating was recorded. Under the conditions of this test, the adductum hexafluorophosphate alone requires greater than 15 min to cure.

TABLE VI:

Organometallic Compound	Cure Time ^a	
	No Onium Salt Added	Onium Salt Added
[CpFe(CO) ₂ Li]	> 600	15
CpFe(CO) ₂ SnPh ₃	> 600	120
CpFe(CO) ₂ GePh ₃	> 600	120
[CpFe(CO) ₂ Li]SnPh ₃	> 600	60
Mn ₂ (CO) ₁₀	> 600	< 15
(CO) ₂ MnSnPh ₃	300	300
(CO) ₂ MnLiSnPh ₃	60	30
Re ₂ (CO) ₉	120	80
[CpRe(CO) ₃ Li] ^b	> 600	30
CpRe(CO) ₃ SnPh ₃	> 600	240

^a time in seconds to cure^b saturated solution < 0.01g dissolved

EXAMPLE 13 (Comparative)

Further examples of the curing of ethylenically unsaturated monomer (25 g of pentamethylol tetraacrylate in 225g acetone) or epoxy monomer (cyclohexene oxide) are provided in a curable composition consisted of 0.01g of the organometallic compound or 0.02g of diphenyl sodium hexafluorophosphate or these same amounts of both compounds added to either monomer. The light sources used were for UV exposure, about 360 nm, two 15 watt GE blackline bulbs and for the visible, a Kodak Carousel Projector for the projector and for the epoxy, the precipitation of the polymer from a 2% ammonia-methanol solution. Free radical systems were purged with N₂ for 2 minutes before and continuously during irradiation while the cationic samples were left open to the air without purging. Sample size was 2 to 3 ml in a 13 x 100 mm Pyrex test tube. The results of these tests are shown in Table VII.

TABLE VII

Photoinitiated Cure Times of Epoxy and Acrylate Compositions ^a		
Curing Agent	Epoxy	Acrylate
[CpFe(CO) ₂ Li]	30 ^b	45
[CpFe(CO) ₂ Li] sodium ^c	30 ^b	45
Mn ₂ (CO) ₁₀	> 180 ^b	> 180 ^b
(CO) ₂ MnSnPh ₃	> 180 ^b	> 180 ^b
(CO) ₂ MnLiSnPh ₃	> 180 ^b	> 180 ^b

^a Cure times given in sec.^b Uninitiated polymer as 10 g methyl acrylate.^c The diphenylsodium salt showed no cure.^d Heat under these same conditions.^e 440 nm filter used with the projector.^f Blackline used as the light source at 440 nm.

EXAMPLE 14 (Comparative)

Examples of the photocuring of ethylenically unsaturated monomer containing organometallic compounds and sodium salt of metal bond containing organometallic compounds and sodium salt of metal bond containing organometallic compounds are provided in a curable composition consisted of 0.01g of the organometallic compound or 0.02g of diphenyl sodium hexafluorophosphate or these same amounts of both compounds added to either monomer. The light sources used were for UV exposure, about 360 nm, two 15 watt GE blackline bulbs and for the visible, a Kodak Carousel Projector for the projector and for the epoxy, the precipitation of the polymer from a 2% ammonia-methanol solution. Free radical systems were purged with N₂ for 2 minutes before and continuously during irradiation while the cationic samples were left open to the air without purging. Sample size was 2 to 3 ml in a 13 x 100 mm Pyrex test tube. The results of these tests are shown in Table VIII.

TABLE IX

Curing of Ethylenically-Unsaturated Monomer and Poly. Epox.		
Compound	Conditions	Results
[CpFe(CO) ₂ Li]	irrad.	30 sec. cure
Mn ₂ (CO) ₁₀	irrad.	30 sec. cure
(CO) ₂ MnSnPh ₃	irrad.	45 sec. cure
(CO) ₂ MnLiSnPh ₃	irrad.	45 sec. cure
Co ₂ (CO) ₈	irrad.	8 min. no cure
Co ₂ (CO) ₈	irrad.	8 min. no cure
Co ₂ (CO) ₈	irrad.	8 min. no cure
Co ₂ (CO) ₈	irrad.	8 min. no cure

EXAMPLE 15 (Comparative)

This example describes the curing of ethylenically unsaturated monomer containing organometallic compounds. Each sample was prepared in a 13 x 100 mm Pyrex test tube. The results of these tests are shown in Table X.

TABLE VIII

Photoinitiated Cure Times of Epoxy and Acrylate Compositions ^a		
Curing Agent	Epoxy	Acrylate
[CpFe(CO) ₂] ₂ b	>100 ^c	>100 ^c
	80°	<5°
[CpFe(CO) ₂] ₂ iodonium ^c	80°	<5°
	>180°	>300°
Mn ₂ (CO) ₁₀	>180°	>100°
	>180°	<10°
Mn ₂ (CO) ₁₀ iodonium ^c	>180°	<10°

^a Cure times given in seconds.

^b Unfiltered projector as light source.

^c The diphenyliodonium salt showed no indication of polymerization by itself under these same conditions.

^d 440 nm filter used with the projector.

^e Blacklie used as the light source, about 360 nm.

EXAMPLE 14 (Comparative)

Examples of the photocuring of ethylenically unsaturated monomers using transition metal-transition metal bond containing organometallic compounds and iodonium salts are given here.

Samples were prepared as 1.0 g methyl acrylate containing 0.01 g metal-metal bond containing complex and 0.015 g Ph₂I⁺PF₆⁻. Up to 0.05 g butadiene or methylene chloride were used to dissolve the photocatalyst systems. Samples were bubbled with N₂ and irradiated using a Kodak Carousel slide projector with a 360 nm cutoff filter and the time required to cure the sample recorded in Table IX. Alternatively, compositions could be cured thermally.

TABLE IX

Curing of Ethylenically-Unsaturated Monomers and Ph ₂ I ⁺ PF ₆ ⁻		
Compound	Conditions	Cure Time
[CpFe(CO) ₂] ₂ b	irrad.	30 sec. slow dark reaction
Mn ₂ (CO) ₁₀	irrad.	30 sec. no dark reaction
[CpFe(CO) ₂] ₂ b	irrad.	45 sec. no dark reaction
[Ru(CO) ₂] ₂ b	irrad.	8 min. no dark reaction
Co ₂ (CO) ₈	irrad.	minutes, slow dark reaction
Co ₂ (CO) ₈	Dark	Cures during deoxygenation

EXAMPLE 15 (Comparative)

This example describes the curing of ethylenically unsaturated monomers with transition metal-metal bond organometallic compounds. Each sample was prepared by dissolving 10 mg catalyst and 20 mg

monomer (25 g of methacrylonitrile) in 100 ml of toluene. The catalysts are provided in Table VIII. 0.02 g of diphenyliodonium hexafluorophosphate was added to the monomer. The light sources used were a 360 nm cutoff filter and the time required to cure the sample recorded in Table IX. Alternatively, compositions could be cured thermally.

dephenylodioxum hexafluorophosphate (if used) in 0.2 g gamma-butyrolactone 2.0 g methyl acrylate (added to remove inhibitor) was added in the dark and nitrogen was bubbled through the sample for 2 min to remove oxygen. Samples were then irradiated in front of a Kodak Carousel Projector containing a 360 nm cutoff filter. If no curing occurred in 15 min, the sample was then irradiated for 15 min under a Helmer Quartz Utility lamp. In Table X, "cure time" refers to the time required for a sample to solidify. Alternatively, compositions could be cured thermally.

TABLE X

Curing of Ethylenically Unsaturated Monomer	Cure time, min
Curing Agent	15 (Helmer)
CpPhiles	6 (Kodak)
CpW(CO) ₂ Me	no cure
CpW(CO) ₂ Me + Iodonium	3.5
CpFe(CO) ₂ + Iodonium ^a	0.5 (dark cure)

^a included for purposes of comparison

EXAMPLE 16 (Comparative)

This example describes the use of [CpW(CO)₂] to cure polyurethane precursors, epoxies or ethylenically unsaturated monomers. Each sample contained 0.01 g [CpW(CO)₂] and 0.02 g dephenylodioxum hexafluorophosphate (if used) in 0.25 g gamma-butyrolactone, to which was added 2.0 g precursor or monomer in a vial. Irradiation was then performed with a Kodak Carousel Projector (8 inches away), modulated with a 360 nm filter. With a urethane precursor stock solution (prepared as in Example 4), in the presence or absence of osmium salt, partial curing to produce a clear solution occurred in 2 hours upon standing in room light for 24 hours; an increase in viscosity occurred. When cyclohexanone was used, and the curing agent consisted of [CpW(CO)₂] and osmium salt, vigorous, endothermic curing occurred within 2 min of irradiation. When methyl acrylate was used as monomer, no curing occurred in the absence of osmium salt. With osmium salt present, the sample became viscous within 4 min and solid within 8 min of irradiation time. Alternatively, these compositions can be cured thermally.

EXAMPLE 17 (Comparative)

To demonstrate the utility of the curing agent for curing of polyurethane precursors, epoxies and vinyl monomers for the case where the organometallic compound contains a single bond between a transition metal and a Group IVA element, the following samples were prepared in a vial: 0.01 g of organometallic compound, 0.02 g of dephenylodioxum hexafluorophosphate (if used, as indicated below), and 0.25 g of gamma-butyrolactone. The samples were gently agitated until dissolution of the organometallic compound was complete. The gamma-butyrolactone was then added in a distance of 2.0 g of polyurethane precursor or monomer was added in reduced light, the vial was capped, and the sample irradiated in front of a Kodak Carousel projector head with a 360 nm cutoff filter at a distance of nine inches, and at room temperature (about 25 °C). Particular details and any experimental variations are indicated in Table X.

TABLE XI

Cure Times: Ph terminated Curing & Polyurethane P Epoxies and Vinyl Monomers 1th Transition Met Group IVA Compounds

Catalyst System	Polyurethane ^a	Epox ^b
[CpFe(CO) ₂] ₂ ^d	120 min (VV) ^e	30 sec
[CpFe(CO) ₂] ₂ /Iodonium ^d	60 min (VV)	3
CpFe(CO) ₂ (CH ₂ Ph)	40 min (V)	12 min
CpFe(CO) ₂ (CH ₂ Ph)/Iodonium	40 min (V)	12 min
CpFe(CO) ₂ (COPh)	120 min (V) ^e	3
CpFe(CO) ₂ (COPh)/Iodonium	120 min (V) ^e	3
CpFe(CO) ₂ (SiPh ₃)	45 min (V) ^h	5 min
CpFe(CO) ₂ (SiPh ₃)/Iodonium	45 min (V) ^h	5 min
CpFe(CO) ₂ (GaPh ₃)	36 min (V) ^h	2.75 min
CpFe(CO) ₂ (GaPh ₃)/Iodonium	36 min (V) ^h	2.75 min
CpFe(CO) ₂ (SnPh ₃)	36 min (V) ^h	2 min
CpFe(CO) ₂ (SnPh ₃)/Iodonium	36 min (V) ^h	2 min
CpFe(CO) ₂ (PbPh ₃)	45 min (V) ^h	3
CpFe(CO) ₂ (PbPh ₃)/Iodonium	33 min (VV) ^h	no cur.

^a no cur.

Group IVA Compounds

Catalyst System	Polyurethane ^a	Epoxy ^b	Vinyl ^c
¹⁰ CpFe(CO) ₂ ^d	120 min (V) ^e	f	no cure
[CpFe(CO) ₂] ₂ /Iodonium ^d	60 min (V)	30 sec	1.8 min
CpFe(CO) ₂ (CH ₂ Ph)	40 min (V)	f	no cure
¹¹ CpFe(CO) ₂ (CH ₂ Ph)/Iodonium	40 min (V)	12 min	23 min
CpFe(CO) ₂ (COPh)	120 min (V) ^e	f	no cure
CpFe(CO) ₂ (COPh)/Iodonium	120 min (V) ^e	5 min	48 hr g
²⁰ CpFe(CO) ₂ (SiPh ₃)	45 min (V) ^h	f	no cure
CpFe(CO) ₂ (SiPh ₃)/Iodonium	45 min (V) ^h	5 min	48 hr g
CpFe(CO) ₂ (GePh ₃)	36 min (V) ^h	f	no cure
CpFe(CO) ₂ (GePh ₃)/Iodonium	36 min (V) ^h	2.75 min	no cure
²¹ CpFe(CO) ₂ (SnPh ₃)	36 min (S) ^h	f	no cure
CpFe(CO) ₂ (SnPh ₃)/Iodonium	36 min (V) ^h	2 min	no cure
CpFe(CO) ₂ (PbPh ₃)	45 min (S) ^h	f	no cure
²² CpFe(CO) ₂ (PbPh ₃)/Iodonium	33 min (V) ^h	no cure	no cure

[illegible][illegible]

- a. Polyurethane precursors are from a stock solution consisting of 23.1 g of DesmodurTM W and 32.6 g of Carbowax 400. Cure times are followed by an indication in parentheses of extent of cure, where V = viscous, WV = very viscous, S = solid.
- b. Monomer is cyclohexene oxide, purified by distillation. Cure time is defined as the time necessary to observe formation of precipitate when one drop of sample is placed in 2 ml of methanol.
- c. Monomer is methyl acrylate, purified prior to use by distillation under reduced pressure. After monomer addition but before irradiation, samples were deoxygenated by bubbling a stream of nitrogen gas through the solution for 2 min, with care being taken to prevent any light from reaching the sample during deoxygenation. Cure is defined by an increase in solution viscosity or a sudden exotherm indicating rapid polymerization (also accompanied by a sudden increase in viscosity).
- d. Included for purposes of comparison to data in other Tables.
- e. 60 min irradiation with Carousel Projector, followed by 60 minutes of irradiation in room (fluorescent) light.
- f. This particular combination was not tested.
- g. 30 minutes irradiation with Kodak projector, following by 30 minutes irradiation under a Hanovia Quartz Utility Lamp (6 inches from bulb), followed by sample storage/irradiation in room (fluorescent) light.
- h. Irradiation with Hanovia Quartz Utility Lamp (15 cm from bulb) in place of the Kodak projector.

EXAMPLE 16

This example illustrates the dual curing of polyurethane precursors and ethylenically-unsaturated monomers using the curing agent [Cp₂et(CO)H]₂ Ph₂ P₂.¹

Sample 1, 25 g in total, was prepared from stock solutions of 2.08 parts DesmodurTM W (4,4'-methylenebis(cyclohexanecarbonyl chloride)), 2.82 parts polytetramethylol (MW = 400), 5.0 parts methyl isocyanate, and 0.06 parts [Cp₂et(CO)H]₂ Ph₂ P₂. To half of the stock solution was added 0.062 parts Ph₂ P₂ (freely dissolved), and 0.06 parts [Cp₂et(CO)H]₂ Ph₂ P₂.

PF₆⁻ Moieties for molybdenum solution dimer = 2.1 MCO₂H = 0.42 mmol/mole of monomer. Samples were irradiated simultaneously using 300 kV x-rays. Molybdenum salt = 1.2%. Samples were then analyzed by 400 MHz ¹H nuclear magnetic resonance spectroscopy. The results are listed in Table XII. Curing agents comprising other combinations of monomers can be used in place of [Co(PhCO₂)₂ and Ph₃P]⁺, respectively.

TABLE XII

Diel Curing of Polyurethane Precursors and Ethylhex-1-ene Unsaturated Monomers			
Oxam Salt	Conditions	Conversion to PU	
		Acrylate	Urethane
Ph ₃ P ⁺	Dark irradiation	0	0
Ph ₃ P ⁺	irradiation, deoxygenated	0	0
None	Dark	24%	0
None	irradiation	0	0
None	irradiation, deoxygenated	0	0

EXAMPLE 10

[illegible]

TABLE 10.10

Coating Agent	Exposure	Acryl. Init.
ICD ₂ /ICD ₃ h	0 ^a	18
ICD ₂ /ICD ₃ h	36	60
ICD ₂ /ICD ₃ h + toluene	<6	<10
Init. ICD ₂ +	<0.8	<0.5
Init. ICD ₂ + toluene	37	4 ^a

^a Wall's values on a 400 MHz instrument.
^b Data collected on the NMR.

As can be seen from the MWD results, the system effectively reduces polymerization immediately. Curing agents comprising zinc carboxylate and oxam salts can be used in place of 1,6-hexanediol and the IOD, e. g.

Dual Curing of Polyurethane Precursors and Ethylenically Unsaturated Monomers			
Oxium Salt	Conditions	Conversion to polymer	
		Acrylate	Urethane
Ph ₃ I	Dark	—	4%
Ph ₃ I	irradiation	78%	56%
Ph ₃ I	irradiation, deoxygenated	78%	8%
None	Dark	0%	11%
None	irradiation	24%	75%
None	irradiation, deoxygenated	trace	10%

This example demonstrates simultaneous curing of ethylenically unsaturated monomers and species. Gelation times will not show that both monomers have reacted at the same time. It is possible to use nuclear magnetic reson. ¹ spectroscopy to differentiate the two polymers in the presence of each other. The experiment was carried out in the following manner: A 1/1, v/v, mixture of methyl acrylate/cyclohexene oxide was prepared. To a 10g sample of this mixture was added 0.01g of [Cp*Fe(CO)₂H] or Me₂Si(CO)₂ diphenylsodium hexafluorophosphate (0.024g with the iron driver 0.003 g with the manganese driver) and it was purged for specified amounts of both components in a small vial was placed 2 ml of the sample and it was purged for 1 min before and continuously during irradiation. The light source was two 15 watt G.E. Deactive bulbs. Irradiation time was 2 minutes. Immediately after completion of the photoex. the Me₂Si in CO₂ was taken. The amount of polymerization was determined by the ratio of the peak intensity of the polymer to that of polymer plus monomer. The results of the study are shown in Table XIII.

Percent Conversion to Polymer from Initiator Study ^a		
Curing Agent	Epoxy	Acrylate
$[\text{Cp}^{\text{R}}\text{Fe}(\text{CO})_2\text{b}]$	0 ^b	18
$[\text{Cp}^{\text{R}}\text{Fe}(\text{CO})_2\text{b} + \text{iododuran}]$	35	80
iododuran	<5	<10
$\text{Mn}(\text{CO})_5$	<0.5	<0.5
$\text{Mn}(\text{CO})_5 + \text{iododuran}$	37	47

As can be seen from the NMR results, the system efficiently initiated both epoxy and free radical polymerization simultaneously. Curing agents comprising other combinations of organosulfonic compounds and osmium salts can be used in place of $[\text{Os}(\text{C}_6\text{H}_5)_2(\text{CO}_2\text{H})_2]$ and $\text{H}_2\text{N}(\text{CO}_2\text{H})_2$ and Ph_3PF_6 , respectively.

EXAMPLE 20

The example demonstrates the simultaneous curing of ethylenically unsaturated and epoxy monomers in a crosslinkable system. The curable composition consists of methyl acrylate, cyclohexene oxide and glycidyl acrylate. If only epoxy or acrylate cure are initiated with a crosslinked insoluble polymer, the polymer is only if both epoxy and acrylate cure are initiated with a crosslinked insoluble polymer.

All monomers were distilled before use. methyl acrylate and glycidyl acrylate from hydroquinone. Samples were carried out under subdued lights. The polymerizable mixture consisted of 0.2 g gamma-butyrolactone, 1.0 g glycidyl acrylate, 5.0 g methyl acrylate and 5.0 g cyclohexene oxide. Depending on the test, added to this were 0.05 g of the desired organometallic compound and/or 0.1 g diphenyliodonium hexafluorophosphate. A 3 g portion of the composition was placed in a glass vial and irradiated between two 15 watt G.E. daylight fluorescent bulbs using an Ultraviolet Products lamp holder (lamp separation distance 4 cm). The sample was purged with nitrogen for one minute preceding and continuously during photocure. The irradiation time required to produce a polymer insoluble in chloroform was recorded, and is noted in Table XIV. Alternatively, these compositions can be cured thermally.

TABLE XIV

Compound	Cure Time*	
	No Onium Salt Added	Onium Salt Added
$\text{CpFe}(\text{CO})_2\text{H}$	>15	1
$\text{CpFe}(\text{CO})_2\text{SnPh}_3$	>15	10
$\text{CpFe}(\text{CO})_2\text{GaPh}_3$	>15	15
$\text{CpFe}(\text{CO})_2\text{bSnPh}_3$	>15	10
$\text{Mn}(\text{CO})_5$	>15	1.5
$\text{Mn}(\text{CO})_5\text{H}$	>15	10
$\text{Co}(\text{CO})_2\text{H}$	>10	4
$\text{Co}(\text{CO})_2\text{bSnPh}_3$	>10	5
$\text{Fe}(\text{CO})_5$	>15	1.5
$\text{CpFe}(\text{CO})_2\text{H}$	>15	10
$\text{CpFe}(\text{CO})_2\text{SnPh}_3$	>15	10

* Time in minutes to produce insoluble crosslinked system
Diphenyliodonium hexafluorophosphate alone under these conditions does not produce a crosslinked system after 15 minutes
b Only 0.01g of the compound used

Claims

1. An energy polymerizable composition comprising at least one ethylenically unsaturated monomer and at least one epoxy monomer.
2. A curing agent comprising (1) an organometallic compound, and (2) an onium salt, and

3. The composition according to claim 1 wherein said organometallic compound has the formula
4. The composition according to claim 1 wherein said organometallic compound has the formula

L¹, L², M

wherein L¹ represents none, or 1 to 12 ligands contributing p-electrons that can be the same or different, L² represents none, or 1 to 12 ligands contributing p-electrons that can be the same or different, M represents none, or 1 to 12 ligands contributing p-electrons that can be the same or different, contributing 2 to 24 p-electrons to the valence shell of M.

L¹ represents none, or 1 to 24 ligands that can be the same or different, contributing 2 to 24 p-electrons to the valence shell of M, L² represents none, or 1 to 24 ligands that can be the same or different, contributing 2 to 24 p-electrons to the valence shell of M, L³ represents none, or 1 to 12 ligands that can be the same or different, each contributing 2 to 24 p-electrons to the valence shell of M.

L¹ represents none, or 1 to 12 ligands that can be the same or different, each contributing 2 to 24 p-electrons to the valence shell of M, L² represents none, or 1 to 12 ligands that can be the same or different, each contributing 2 to 24 p-electrons to the valence shell of M, L³ represents none, or 1 to 12 ligands that can be the same or different, each contributing 2 to 24 p-electrons to the valence shell of M.

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1-1-77

selected from substituted and unsubstituted acyclic and cyclic unsaturated hydrocarbons, substituted and unsubstituted aromatic compounds, each capable of being substituted with one or more substituents, and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of being substituted with one or more substituents. The number of substituents contributing to the valence shell of M₁ is 24. Contributions to the valence shell of M₂ are different contributing an even number of substituents.

contributing 2 to 24 ligands that can be the same or different, each donating 2, 4, or 6 sigma-electrons; c) represents mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons selected from mono-, di-, and tri-dentate ligands, each contributing no more than 2 to the valence shell of M.

and 13 can be bridging or non-bridging ligands:

[illegible]

The composition according to claims 1 and 2 wherein said oxonium salt has the formula II

AX is an anion, cation, or diazonium cation, and A is an anion, cation, or diazonium cation.

4. The composition according to claims 1 to 4 wherein said ethylenically-unsaturated monomer is an organic sulfonate counterion, or a macroanionically substituted monomer.

5 The composition according to claims 1 to 4 wherein said polyurethane preoligomer contains at least two isocyanate-reactive hydrogen atoms where the

of polyisocyanates and carbamate groups. The concentration of isocyanate-reactive hydrogen atoms is in the range 1.2 to 2.0, and the concentration of carbamate groups is in the range 0.5 and 1.0.

6 A process comprising:
a) providing a polymerizable mixture according to claims 1 to 5;
b) allowing said mixture to polymerize or adding energy to said mixture to effect polymerization;
c) coating on one surface thereof the polymerized mixture.

7 A layered structure comprising a substrate having coated thereon a layer of the material of claim 1 to 5.

6 The layered structure according to claims 1 to 5
9 A shaped article comprising the composition according to claims 1 to 5 and 7 to 9 which has been cured

10 The composition according to claim 1, wherein the polymer is a polyether ether ketone.

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<http://jme.sagepub.com>

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 5. *What are the conclusions of the study?*

1. *Pharmaceutical industry*—United States—History. I. Title. II. Series.

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[illegible]

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23

1. *Pharmaceutical industry* – The pharmaceutical industry is a major player in the healthcare sector, responsible for the development, production, and distribution of drugs. It is a highly regulated industry with significant barriers to entry, including high R&D costs and complex regulatory requirements. The industry is characterized by a high degree of concentration, with a few large firms dominating the market.

[illegible]

TABLE V

10
Photoinitiation of Epoxies: Use

Photocrosslinking of Epoxy Resin		
Compound	Cure Time*	
	No. Drosses Salt Added	Grum Ashes
[Cofe(CO) ₂ :L	>10	1
Cofe(CO) ₂ :SnPr ₃	>10	5
Cofe(CO) ₂ :CaPr ₃	>10	5
[Cofe(CO) ₂ :L:SnPr ₃	>10	1
Mn ₂ (CO) ₈	>10	4
(CO) ₂ Mn(SnPr ₃) ₂	>10	4
[(CO) ₂ :Mn(SnPr ₃) ₂	>10	3
Re(CO) ₅ :H ₂ O	1	4
Co(CO) ₈ :SnPr ₃	1	4

*Time in minutes to use

1. The following are the main features of the Indian Constitution:

EXAMPLE 11

To further demonstrate the activity of the organometallic catalyst, another assay and catalyst composition. The organometallic catalyst was previously in presence of an epoxy or acrylate. The free acrylate was distilled from hydroquinone and stored (and until used) obtained from Aldrich. The organometallic compounds were Diphenylcarbamoyl hexafluoroisopropylidene was recrystallized from a done as 100% solids except as noted in a small vial was packed 0.02 g of the organometallic with, set along with 2 g of the epoxy monomer. For the acrylate tests, set before and continuously during the polymerization. The epoxy test, open to the air. The light source was on 15 and 30 minutes. The lines represent the time required to reach the same. Alternatively, the acrylate compositions can be cured thermally.

Alternatively, the affiliate companies can

1. *Introduction*
 2. *Background*
 3. *Methods*
 4. *Results*
 5. *Discussion*
 6. *Conclusion*
 7. *References*
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1. *Phragmites australis* (Cav.) Trin. ex Steud.

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the 1990s, the number of people in the world who are illiterate has increased from 1.2 billion to 1.5 billion. The number of illiterate people in the world is projected to reach 1.7 billion by the year 2015. The number of illiterate people in the world is projected to reach 1.7 billion by the year 2015.

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